

# Non-invasive identification of surface materials on marble artifacts with fiber optic mid-FTIR reflectance spectroscopy

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## Abstract

Research work using a compact and portable fiber optic mid-infrared reflectance spectrometer has been carried out to study surface materials on marble, first on laboratory reference models and then on historical objects. The laboratory research has shown that the complex optical reflectance phenomena of layered samples can be interpreted in terms of the nature of the compounds present (sulfates, oxalates, phosphates, resins, waxes and proteins were studied) even with a very low signal overlapping with the strong carbonate reflectance. The portable instrument was used for in situ examination of the surface condition of two Italian marble works of art: the *Deposizione dalla Croce* by Benedetto Antelami in the Parma cathedral and the *David* by Michelangelo in the Galleria dell'Accademia in Firenze.

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## 1. Introduction

The understanding of the conservation conditions of a work of art is of primary importance for the development of an appropriate conservation intervention. The identification of contaminants and alteration products and their distribution on the marble surface is typically part of the analytical investigation carried out in preparation for a conservation plan.

It is well known that the main alteration affecting a marble surface, exposed to a typical urban environment, is the transformation of calcite to calcium sulfate and calcium nitrate due to the interaction with air born SO<sub>2</sub> and NO<sub>2</sub> in presence of humidity. Another typical mechanism of alteration is the deposition of particulate, such as sulfates, nitrates, phosphates, chlorides and other pollutants present in the atmospheric aerosols [1–4]. In addition, organic contaminants can easily be present on a marble surface as residues of biological attacks or past treatments with natural polymers, such as waxes and proteins or synthetic products, such as siloxanes and acrylic resins [1].

Conventional analytical techniques for identifying patinas and incrustations include scanning electron microscopy, X-ray diffraction, ionic chromatography and transmission infrared spectroscopy [5]. These are all invasive investigations requiring the removal of small fragments of the artefact. Portable and non-contact equipments allow scientists to respect the integrity of the artwork while collecting widespread analytical measurements that can provide an extensive panorama of the surface condition and that can be repeated at any time.

Non-invasive investigations of outdoor stone monuments have been carried out using portable X-ray fluorescence (XRF) for sulfur and chlorine identification while portable near-infrared spectroscopy coupled with principal component analysis has been used for the identification of sulfate and oxalate alterations [6–8].

This paper illustrates the capabilities of fiber optic FTIR reflectance spectroscopy in the medium infrared (mid-FTIR) in the in situ and non-contact identification of a large variety of inorganic and organic materials often included in incrustations and patinas on marble surfaces. The study has mainly focused on the identification of sulfates, phosphates, nitrates, oxalates, proteins, waxes, acrylic resins and siloxanes; all materials that are commonly found on Italian monuments made with *Carrara*

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marble resulting from natural weathering and past treatments [9].

The work is divided in laboratory testing and in situ applications. The aim of the laboratory measurements was to use simulated marble models with known surface contaminants to evaluate the potential of mid-FTIR portable set-up to detect different substances having main bands that overlap the strong carbonate signal of marble. After laboratory testing and evaluation, the set-up was applied to two case studies of Renaissance sculpture masterpieces: the Antelami's bas-relief *Deposizione dalla Croce* in the Parma's cathedral and the Michelangelo's *David* in the Galleria dell'Accademia in Firenze. In the first case, the mid-FTIR portable set-up allowed to identify a wide contamination of oxalates, silicates and sulfates and a past protective layer made of proteinaceous and lipidic components. In the second case, besides the presence of oxalates and sulfates also beeswax residuals have been detected.

## 2. Experimental

### 2.1. Apparatus

Reflectance mid-FTIR spectra were recorded using a portable JASCO VIR 9500 spectrophotometer equipped with a Remspec mid-infrared fiber optic sampling probe. The bench is made up of a Midac Illuminator IR radiation source, a Michelson interferometer and a liquid nitrogen cooled Mercury Cadmium Telluride (MCT) detector. The equipment is portable weighing only 35 kg and with overall dimensions of 50 cm × 50 cm × 50 cm. It can be easily moved into museum rooms as well as up onto scaffoldings. The fiber optic probe is a bifurcated cable containing 19 chalcogenide glass fibers, 7 of which carry the infrared radiation from the source to the sample, while the other 12 collect the radiation reflected off the surface. The chalcogenide glass fibers allow the collection of spectra in the range 4000–900 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. The spectra show an excellent signal-to-noise ratio throughout the range, apart the 2200–2050 cm<sup>-1</sup> region due to the chalcogenide Se–H stretching absorption. The fiber optic probe is kept strictly perpendicular to the samples surface (normal geometry) by a mechanical arm. The distance between the probe tip and the surface is fixed at about 5 mm avoiding contact between the fibers and the artwork. The width of the investigated area is determined by the probe diameter, which is about 4 mm. The total reflectivity,  $R$ , due to the combined diffuse and specular components, is measured using the spectrum from an aluminum mirror plate as background. The spectrum intensity was defined as the pseudo absorbance  $A'$ , where  $A' = \log(1/R)$ .

### 2.2. Procedure

Quarry Carrara marble simulated models, with surface dimension 5 cm × 5 cm, were carefully polished using a P1000 polishing paper and then covered with thin layers of one material. Simulated models of patinas were made with wax, casein, polyacrylic resin, siloxane, while simulated models of incrustations were made with depositions of sulfate, oxalate, phosphate and

nitrate. The simulated patina models were prepared by brushing as follows: (a) melted beeswax (Phase), diluted with Turpentine essence (Zecchi); (b) casein (Zecchi); (c) poly(EMA/MA) 70/30 (Paraloid® B72, Rohm and Haas) diluted with acetone; (d) alkyl silicic resin (Silirain® 50, Rhodia Siliconi Italia). The simulated incrustation models were prepared by controlled deposition from salt solutions of (a) calcium sulfate dihydrate (99.0%, Fluka); (b) sodium phosphate (96%, Aldrich); (c) calcium nitrate (99.0% Aldrich); (d) sodium oxalate (99.5%, Riedel-de Haën). Depositions of salts were carried out putting saturated solutions on the Carrara marble blocks and letting them dry at room temperature for some days. These applications were repeated several times to achieve depositions ranging from about 0.1 to 10 μmol/cm<sup>2</sup>. Five reflectance mid-infrared spectra were collected randomly on the 5 cm × 2 cm area, of each simulated model. These spectra were averaged to obtain one representative spectrum for each model surface, the standard deviation of absorbance has been calculated. The limit of detection (LOD) is defined as the lower salt concentration that produces a band in the reflectance infrared spectrum in that is three times the baseline noise level.

## 3. Results and discussion

Marble is made primarily of the mineral calcite, whose spectroscopic properties in the mid-infrared spectral region are well known [10]. Among the three mid-infrared internal fundamental modes, only the  $\nu_3$  asymmetric stretching of CO<sub>3</sub><sup>2-</sup> lays in the region of interest 4000–900 cm<sup>-1</sup>. Fig. 1 shows the reference reflectance spectrum of calcite measured by the portable mid-FTIR equipment. The spectrum was recorded on a natural mineral sample of calcite with an external surface obtained by cleavage. The calcite surface provides a distorted (mixed mode) spectrum: a convolution of the refractive index ( $n$ ) and absorption coefficient ( $k$ ) ruled out by the Fresnel law. In particular, due to its strong absorption coefficient  $k$ ,  $\nu_3$  band (at about 1400 cm<sup>-1</sup>) appears as a maximum of reflectance rather than a minimum, following the so-called *reststrahlen* effect. In addition, the calcite *reststrahlen* band shows a very large splitting

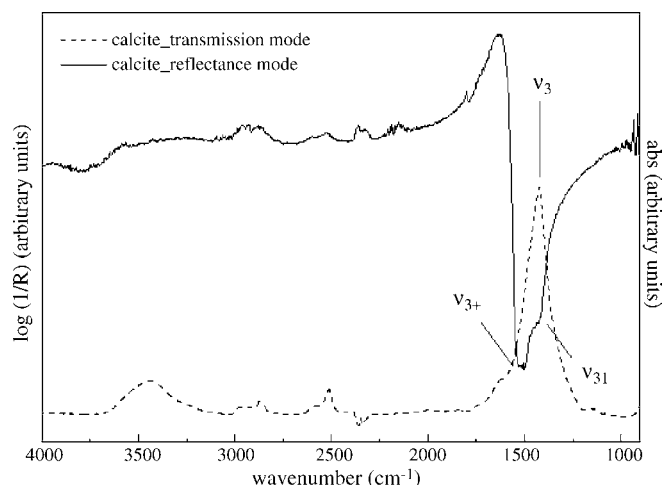


Fig. 1. Mode distribution and selection rules for calcite structures.

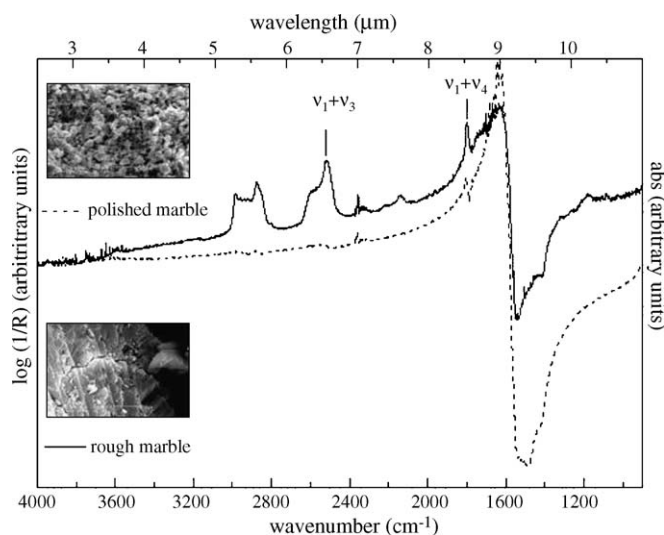


Fig. 2. Reflectance spectra collected on polished and rough porous marble surfaces; microphotos of samples surface roughness observed by SEM (magnification about  $\times 3000$ ).

of the transverse and longitudinal component of the vibration ( $\Delta_{LO-TO} = 100 \text{ cm}^{-1}$ ). Working on marble slabs, the reflectance features of calcite results to be strongly affected by the surface roughness. The surface highly contributes to the specular light reflection when the dimension of the hills and valleys of the marble roughness are greater than the wavelength of the light (as shown in Fig. 2, on the spectrum collected on a polished marble surface). On the contrary, for roughness of similar dimension of the wavelength (that is 2–11  $\mu\text{m}$ ), the amount of specular reflection is lower and, as a consequence, the spectrum shows a swallowing of the  $\nu_3$  *reststrahlen* band (as shown in Fig. 2, spectrum collected on a fine-grained surface with a sugary texture). In the latter case, besides the first order internal mode, bands at 1798 and 2515  $\text{cm}^{-1}$  are clearly observed and assigned to the calcite combination modes  $\nu_1 + \nu_4$  and  $\nu_1 + \nu_3$ , respectively [11]. The research work presented here, mainly focused on the identification of incrustations and patinas commonly present on marble monuments and resulting from weathering and/or past interventions. Generally, the characteristic vibrations of contaminants, in the patina and/or in the incrustations, overlap with the strong reflectance of the calcite substrate making the contaminant identification challenging. As shown in the rest of this paper, mid-FTIR reflectance spectroscopy allows the identification of many substances in spite of this problem.

Fig. 3a illustrates a first example of patina identification: the spectrum of casein treated models is shown in Fig. 3a. Here, casein is used as model for proteinaceous patinas, frequently encountered on the surface of a marble monument due to past maintenance operations carried out by conservators [9]. Although the spectral features are quite complex, resulting as the sum of substrate and patina signals, two bands showing a derivative shape can be assigned to the protein: the amides I and II stretching at 1650 (C=O stretch) and 1545  $\text{cm}^{-1}$  ( $\text{NH}_2$  deformation), respectively [12]. The amide III band (at about 1450  $\text{cm}^{-1}$ ) is barely resolved due to the overlap with  $\nu_3$  *reststrahlen* band of the matrix.

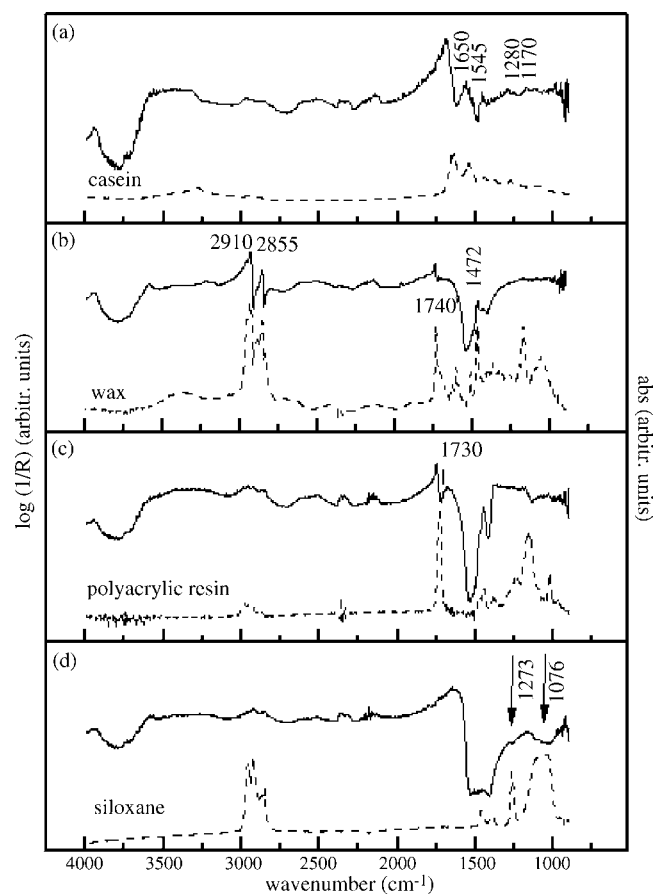


Fig. 3. Reflectance spectra of (a) a casein treated model compared with the transmission spectrum in KBr micropellet of casein; (b) a wax treated model compared with the transmission spectrum in KBr micropellet of wax; (c) a polyacrylic treated model compared with the transmission spectrum of Paraloid® B72; (d) a siloxane treated model compared with the transmission spectrum of Silirain® 50.

Fig. 3b presents the spectrum of beeswax, another substance frequently used in past restoration treatments to protect the marble surfaces. Typical bands of beeswax (2910 and 2855  $\text{cm}^{-1}$  C–H stretching, 1740  $\text{cm}^{-1}$  C=O stretching, 1472  $\text{cm}^{-1}$  C–H deformation, 1175  $\text{cm}^{-1}$  C–O stretching) are clearly distinguishable from those of the substrate. In particular, both C–H stretchings and C=O stretching show a derivative shape, owing to their strong absorption coefficient.

Fig. 3c and d present spectra collected on samples treated with two different synthetic protective agents: polyacrylic resin (Paraloid® B72) and alkyl siliconic resin (Silirain® 50). The poly(EMA/MA) can easily be identified by the main absorption at 1730  $\text{cm}^{-1}$ , assigned to the stretching of the C=O ester group [13] (see Fig. 3c), while the Si–O stretching, distinctive for a siloxane protective, is present with *reststrahlen* bands at 1273 and 1076  $\text{cm}^{-1}$  (see Fig. 3d).

Fig. 4a illustrates the results on inorganic incrustations; the phosphates are clearly identifiable by the presence of three *reststrahlen* bands at 1148, 1068 and 990  $\text{cm}^{-1}$  assigned to phosphate anion stretchings. The LOD was determined by artificial depositions in the laboratory and, for phosphates, resulted to be 1.1  $\mu\text{mol}/\text{cm}^2$ . Surprisingly, as shown in the insert of

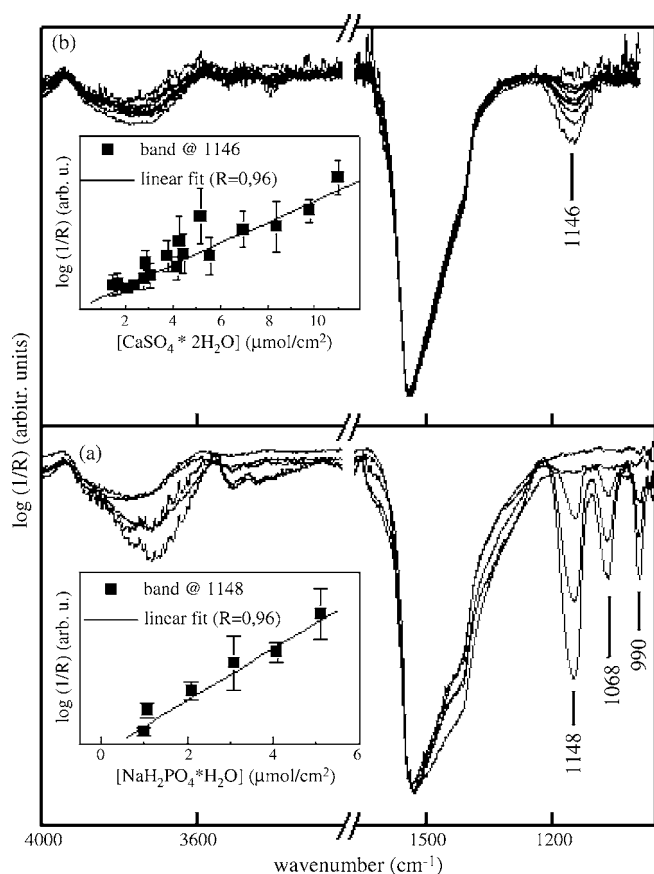


Fig. 4. Reflectance spectra of marble models treated with (a) phosphate and (b) sulfate solutions at different concentration and relative plots of reflectance intensity vs. salt concentration.

Fig. 4a, the plot of pseudo absorbance  $A'$  of the band at  $1148\text{ cm}^{-1}$  versus the salt concentration shows good linearity with regression coefficient  $R$  equal to 0.96. The intensity had been calculated normalizing all the spectra to the  $\nu_3$  band of calcium carbonate. Even if the reflectance in the normal ( $0^\circ/0^\circ$ ) geometry mode results in spectral distortions, a linearity is evident in the limited concentration range explored.

Fig. 4b shows that identification of gypsum is possible using the band at  $1146\text{ cm}^{-1}$  (asym stretching of sulfate), characterized by a *reststrahlen* shape. The LOD is  $1.5\text{ }\mu\text{mol/cm}^2$  and it is greater than that found for phosphates. Also in this case, a linear trend of reflectance versus concentration has been observed (see insert of Fig. 4b) within the limited concentration range examined.

In the case of oxalate simulated marble model, it has been possible to establish the LOD at  $5.2\text{ }\mu\text{mol/cm}^2$  but without a linear correlation between the reflectance and the concentration. This could be attributed to reflectance distortions but also to the superposition of the oxalate stretchings ( $1320$  and  $1600\text{ cm}^{-1}$ ) to the  $\nu_3$  fundamental band of calcium carbonate. Among the various laboratory tests illustrated above, only the identification of nitrates was not successful, due to the large overlap of the relevant diagnostic N–O stretching of calcium nitrate with that of C–O of calcium carbonate.

Table 1

Main diagnostic band for organic patinas and inorganic incrustations

Compound	Diagnostic bands ( $\text{cm}^{-1}$ )	Mode assignment
$\text{CaCO}_3$	1400 (inverted)	$\nu_3$
	1798	$\nu_1 + \nu_4$
	2515	$\nu_1 + \nu_3$
Casein	1650	Amide I
	1545	Amide II
Beeswax	2910 and 2855 (derivative)	$\nu(\text{CH})$
	1740 (derivative)	$\nu(\text{C=O})$
	1472	$\delta(\text{C-H})$
	1175	$\nu(\text{C-O})$
Polyacrylic resin	1730	$\nu(\text{C=O})$
Alkyl siliconic resin	1273 and 1076	$\nu(\text{Si-O})$
$\text{Ca}_3(\text{PO}_4)_2$	1148, 1068 and 990 (inverted)	$\nu(\text{PO}_4^-)$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1146 (inverted)	$\nu_a(\text{SO}_4^-)$
$\text{Na}_2\text{C}_2\text{O}_4$	1320	$\nu_s(\text{C-O}) + \delta(\text{O-C=O})$
	1600	$\nu(\text{C=O})$

A summary of infrared diagnostic features of organic patinas and inorganic incrustations analyzed in reflectance mode on a carbonate matrix is reported in Table 1.

### 3.1. In situ studies of original marble artworks

After the instrument's assessment with laboratory research on simulated models, the mid-FTIR has been used on site on marble masterpieces, as part of the diagnostic investigation required for planning conservation intervention and preventive conservation. The Antelami's *Deposizione dalla Croce* (deposition from the cross). This marble bas-relief, located in the transept of the Parma Cathedral, is signed and dated by Benedetto Antelami (1150–1230) and is regarded as one of his most important pieces. Measure with mid-FTIR on this bas-relief showed several bands due to superficial inorganic and organic contaminants, in addition to the expected spectral features of the marble substratum. Surface contaminants include first of all oxalates distributed homogeneously on the surface. Fig. 5a shows a typical spectrum (collected on the *Sinagoga* vexillum, in the central part of the bas-relief) with the characteristic absorption bands of oxalate: C=O stretching, combined with H–O–H bending of crystallization water, at  $1622\text{ cm}^{-1}$  and C–O stretching at  $1319\text{ cm}^{-1}$ . Both oxalate absorption bands appear inverted due to the *reststrahlen* effect. In addition to oxalate, a diffused presence of silicates and sulfates is visible by mid-FTIR. Fig. 5b clearly shows the band at  $1016\text{ cm}^{-1}$  due to the stretching of  $\text{SiO}_4^{4-}$  together with that at  $1140\text{ cm}^{-1}$  due to the stretching of  $\text{SO}_4^{2-}$ . Both the absorptions are distorted by *reststrahlen* effect and appear as negative bands. Notably, the bands of sulfate and silicate show a relative intensity quite constant all over the bas-relief surface suggesting that these two inorganic contaminants may be related and possibly due to dry deposition of atmospheric dust.

Finally, the presence of organic patinas can be observed even if the bands obtained are distorted by reflectance effect and overlapped with the strong marble substratum absorption.

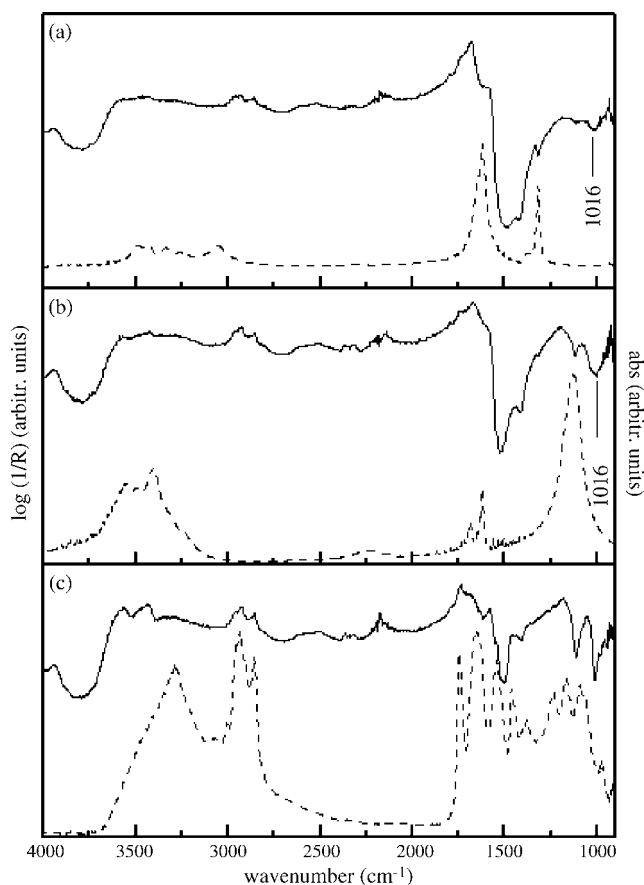


Fig. 5. *Antelami's Depositione dalla Croce*: reflectance spectra collected from the marble surface of (a) the *Sinagoga* vexillum, compared with the transmission spectrum of standard calcium oxalate monohydrate; (b) the angel, compared with the transmission spectrum of standard gypsum; (c) Giuseppe of Arimatea, compared with the transmission spectrum of standard egg yolk.

Fig. 5c shows the spectrum collected on the figure of *Giuseppe of Arimatea* with a C=O stretching due to a lipid component ( $1735\text{ cm}^{-1}$ ), a C=O stretching of amide (amide I at  $1640\text{ cm}^{-1}$ ), a N–H bending of amide (amide II at  $1540\text{ cm}^{-1}$ ), a C–H bending ( $1467\text{ cm}^{-1}$ ) and C–O bending of an esteric bond. All these observations suggest the presence of lipid and proteinaceous components, which may be the results, as a reliable hypothesis, of a surface application of a protective used in the past to give more brilliance to the surface.

*The Michelangelo's David.* An extensive model project of preventive conservation was developed in occasion of the recent conservation (2004) of the Michelangelo masterpiece. The project was coordinated by the *Opificio delle Pietre Dure* (Firenze) and aimed at developing appropriate cleaning methods and future monitoring and maintenance procedures for this work of art [14]. The first step was the assessment of the marble surface condition using several non-invasive investigations. Within this project, an in situ study by mid-FTIR spectroscopy was carried out and different kinds of contaminations were identified. Sulfates were clearly detected on residual black crusts on the right hand forefinger (see spectrum in Fig. 6a) as well as on grey incrustations for instance, on the right foot and the right part of the chest. Traces of sulfates were also found in

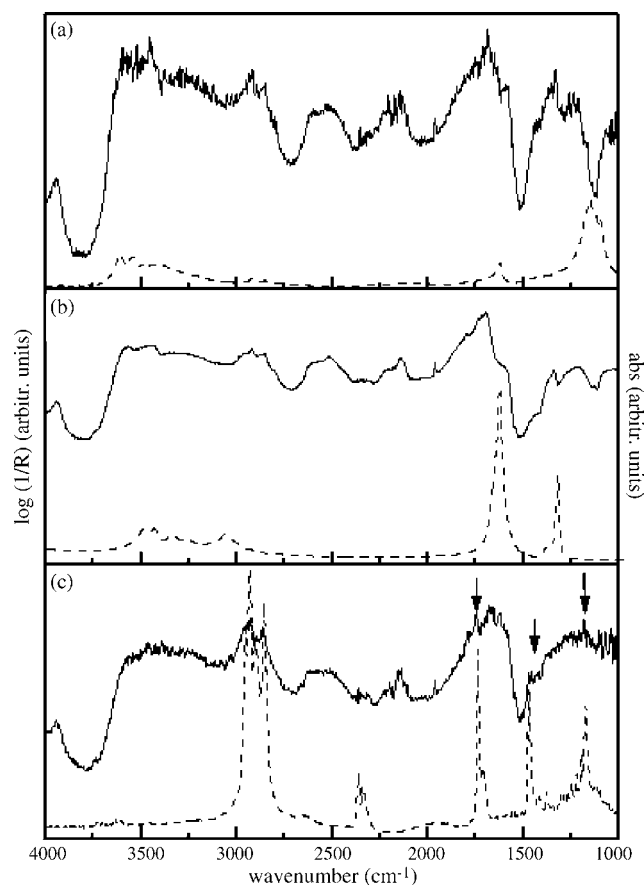


Fig. 6. *Michelangelo's David*: (a) reflectance spectrum collected from residual black crust on forefinger; (b) reflectance spectrum collected from on the left foot; in black dash line absorbance spectrum of standard calcium oxalate is reported; (c) reflectance spectrum collected on the right thigh; in black dash line absorbance spectrum of standard beeswax is reported. The arrows indicate the diagnostic bands of wax.

areas that appeared not macroscopically altered (see spectrum in Fig. 6b). This indicated that a sulfate contamination, greater than few  $\mu\text{mol}/\text{cm}^2$ , is diffused over the statue's surface, with higher concentration on specific zones. The sulfates were attributed to gypsum, which may be present on the surface due to dry indoor deposition or to residues of the substances used during the casting of the David in 1847. Oxalates were also identified often, but not always, on yellowish patinas, as shown in the spectrum in Fig. 6b collected for the left foot. Contrary to the sulfates, the oxalates were localized in the lower part of the statue. It is difficult to explain this distribution, but possibly the effect of rain dilavation could have affected the higher part of the sculpture when in its original open air location, leaving the lower part richer in oxalates. Finally, spectral features of organic components (mainly C=O and C–H stretching) were detected in some spectra. The identification of the organic component has been attempted for spectral features well resolved and from the marble substrate absorption (see Fig. 6c). Based on the spectra recorded on laboratory models, the organic component was identified as beeswax. It may either be a residue of the detachment additives used during the casting or a residue of old protective substances. Contrary from the lab models, the in situ spectra on the David did



not show derivative features of C–H and C=O stretching, owing to the lower amount of wax patina; for this reason the absorption wavenumbers are in quite good agreement with those acquired in transmittance, as is visible in Fig. 6c. While most recorded mid-FTIR spectra showed the presence of surface material, some collected in specific areas, such as the top of the head, the right cheek and the left calf did not show any detectable contamination.

#### 4. Conclusions

This paper illustrates the high potential of in situ mid-FTIR spectroscopy for qualitative identification of alterations and contamination on marble artworks. The optimum performances of a compact fiber optic Fourier transform spectrophotometer have been shown for non-contact measurements. The technique is well suited to detect common organic patinas (protein, wax, oxalates, acrylic resins [13], siloxanes) as well as inorganic incrustation (sulfates and phosphates) and has a good limit of detection (about 1.1–1.5  $\mu\text{mol}/\text{cm}^2$ , determined for inorganic salts). In situ non-contact mid-FTIR measurements offer to conservation scientist's new opportunities for the assessment of degradation in monuments and for monitoring activity as part of preventive conservation programs. Indeed, significant and rele-

vant diagnostic information can be achieved without the removal of any sample and with immediate, on-line results.

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